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## RADIOACTIVITIES IN RETURNED LUNAR MATERIALS AND IN METEORITES

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Grant NAG 9-42

Semiannual Progress Reports No. 6 & 7

For the period 1 August 1985 through 31 July 1986

Principal Investigator  
Dr. Edward L. Fireman

August 1986

Prepared for  
National Aeronautics and Space Administration  
Johnson Space Center  
Houston, Texas

Smithsonian Institution  
Astrophysical Observatory  
Cambridge, Massachusetts 02138

The Smithsonian Astrophysical Observatory  
is a member of the  
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The NASA Technical Officer for this grant is Dr. I. D. Browne, Code SN2, Lyndon B. Johnson Space Center, Houston, Texas 77058.

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During the past 12 months we carried out a preliminary carbon-14 study on lunar soil with the University of Toronto Iso Trace accelerator mass spectrometer (Attachment 1). This accelerator was recommended to us for our  $^{14}\text{C}$  work by Dr. R. Schneider of A.S. and E., who was the field engineer during the assemblage and start-up operation of the accelerator. After our preliminary study using  $\text{CO}_2$  from 10084,937 soil, which had previously been counted with low-level mini-proportional counters, it became clear to me that the Toronto accelerator could carry out  $^{14}\text{C}/^{13}\text{C}/^{12}\text{C}$  ratio measurements on 1 gram meteorite and lunar samples and that the  $^{14}\text{C}$  measurements are done with higher precision and better reliability than elsewhere. I instituted a collaborative program with the University of Toronto Iso Trace accelerator group, which I expect will be scientifically fruitful. Arrangements have been made for Dr. R. P. Beukens of the Toronto Accelerator Group to spend time in our laboratory-extracting the carbon compounds from Antarctic meteorite and lunar samples and converting the compounds to  $\text{CO}_2$ .

During the past two years, we developed a uranium-series dating method for polar ice and are applying this method to ice from the Allan Hills site, Byrd core, and the Beardmore glacier. Our publications during the past 12 months (Attachments 2, 3, 4, 5 and 6) have been mainly in this area.

## Attachments

1. Carbon-14 in Lunar Soil by Accelerator Mass Spectrometry, R. J. Schneider, E. L. Fireman, R. P. Beukens, and W. E. Kieser, submitted to Journal of Geophysical Research, April 25, 1986.
2. Uranium-Series Dates for Ice from Two Allan Hills Locations (abstract), E. L. Fireman, Lunar and Planetary Science XVII, Part 1, p. 226, 1986.

3. Uranium Series Dating of Allan Hills Ice, E. L. Fireman, Journal of Geophysical Research, Vol. 91, No. B4, p. D539, 1986.
4. Correction to "Uranium Series Dating of Allan Hills Ice," E. L. Fireman, Journal of Geophysical Research, Vol. 91, No. B8, p. 8393, 1986.
5. Uranium-Series Study of Ice near the Bottom of the Byrd Core, E. L. Fireman (abstract), submitted to the September 22 to 25, 1986 Meeting of the Meteoritical Society.
6. Uranium-Series Dating of Antarctic Ice, submitted to Antarctic Journal of the United States, May 1986.

**ATTACHMENT 1**

ASE-5118

Carbon-14 in Lunar Soil by Accelerator Mass Spectrometry

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### Abstract

The  $^{14}\text{C}/^{12}\text{C}$  ratios in the carbon released from 1.00 g of lunar soil 10084.937 (74-125  $\mu\text{m}$  grain size) at 400, 600, 800 and 1000°C were measured with the University of Toronto IsoTrace Laboratory's accelerator mass spectrometer. The  $^{14}\text{C}/^{12}\text{C}$  ratios increased monotonically with increasing temperature from  $(0.436 \pm 0.012) \times \text{modern}$  at 400°C to  $(2.236 \pm 0.048) \times \text{modern}$  at 1000°C. The carbon released from lunar soil below 1300°C is thought to contain solar wind implanted carbon and no spallation carbon-14 produced by the action of cosmic rays. If this is true, then it is difficult to explain the  $^{14}\text{C}/^{12}\text{C}$  ratio of  $2.236 \times \text{modern}$  without invoking a  $^{14}\text{C}/^{12}\text{C}$  abundance in the solar wind of at least  $2.63 \times 10^{-12}$ .

## Introduction

The University of Toronto IsoTrace accelerator mass spectrometer facility [Beukins et al., 1986; Kieser et al., 1986] offers the possibility of high sensitivity  $^{14}\text{C}/^{12}\text{C}$  ratio measurements on small ( $\pm 1 \text{ cm}^3$  STP) samples of  $\text{CO}_2$ . This was used to analyze the carbon extracted from lunar soil. The carbon contents of lunar soils are large (100-300 ppm) compared to those in lunar rocks (5-10 ppm); furthermore, the extraction of carbon from lunar rocks requires above-melting temperatures ( $\geq 1300^\circ\text{C}$ ) while extraction of carbon from lunar soils occurs at much lower temperatures. Chang et al. [1972, 1973], Gibson and Moore [1973], and Simoneit et al. [1973] showed that the carbon compounds in lunar soils are released principally between 500 and 1200°C and interpreted both the amounts and the temperature-release patterns as resulting from carbon implantation. Solar wind is the likely source of the excess carbon implanted in lunar soil. An important question can be addressed by accelerator mass spectrometry: What is the  $^{14}\text{C}/^{12}\text{C}$  ratio in the recent solar wind implanted in lunar soil? In spite of considerable effort, the isotopic composition of the solar wind carbon is uncertain. Studies of carbon-14 extracted from surface lunar soils [Fireman, 1978], which indicated the presence of carbon-14 in recent solar wind, were limited by the sensitivity of the mini-proportional counters used.  $^{13}\text{C}/^{12}\text{C}$  ratio studies [Becker, 1980; Norris et al., 1983] on the carbon extracted from lunar soils were uncertain because of possible terrestrial contamination. Lunar samples also contain spallogenic carbon-14 produced by the action of cosmic rays on the most abundant elements, principally oxygen. The spallogenic carbon-14 is difficult to extract by pyrolysis, requiring above-melting temperatures [Fireman,

1978]. The carbon-14 released below 1300°C must therefore be attributed to another source, either solar wind or contamination with terrestrial carbon.

A suite of  $\text{CO}_2$  samples, which had been prepared by stepwise, 400, 600, 800, 1000°C temperature extractions from the 74 to 125  $\mu\text{m}$  size particulates of lunar soil, 10084, were available. These  $\text{CO}_2$  samples had been counted for carbon-14 with low-level proportional minicounters [Fireman, 1978]. We reanalyzed these samples with the IsoTrace accelerator mass spectrometer and compared the results.

#### Sample Preparation

The history of the  $\text{CO}_2$  samples is as follows. A 1.00 g sample of lunar soil labeled 10084.937, which had been sieved into the 74 to 125  $\mu\text{m}$  size range by King [1971], was received by Fireman [1978]. He placed the sample in a degassed molybdenum crucible and evacuated it overnight at room temperature. The temperature of the sample was raised by resistance heating and then held constant for 4 hours while the evolved gas was collected with an automatic Toepler pump. The temperatures used were 400, 600, 800, and 1000°C. The collected gas was passed over  $\text{CuO}$  at 650°C and the carbon compounds were converted to  $\text{CO}_2$ . The amounts of  $\text{CO}_2$  obtained were  $0.95 \text{ cm}^3$  (STP) at 400°C,  $0.60 \text{ cm}^3$  (STP) at 600°C,  $0.77 \text{ cm}^3$  (STP) at 800°C, and  $0.224 \text{ cm}^3$  (STP) at 1000°C. After radon was removed from the  $\text{CO}_2$ , argon was added. The gas mixture was placed in a small proportional counter and counted for carbon-14. After several months of counting, the gas was removed from the counter and stored in glass bulbs.

During the past year, we decided to have these samples reanalyzed with the Toronto accelerator mass spectrometer. The gas was removed from the bulbs and the  $\text{CO}_2$  separated from the argon by freezing the  $\text{CO}_2$  in a cold trap at liquid  $\text{N}_2$  temperature. The amounts of  $\text{CO}_2$  recovered are given in

the second column of Table 1. These amounts were smaller than those commonly used in the IsoTrace sample preparation; therefore carrier "tank"  $\text{CO}_2$  was added to increase the volumes to about  $8 \text{ cm}^3$  (STP). The amounts of carrier  $\text{CO}_2$  added to the samples are given in the third column of Table 1. This "tank"  $\text{CO}_2$  had been counted for  $^{14}\text{C}$  in a large volume counter, giving greater than  $40 \times 10^3$  year age; and its  $\delta^{13}\text{C}$  had been measured to be -43.3 per mil by conventional mass spectrometry.

The  $\text{CO}_2$  samples were sealed in glass bulbs and taken to Toronto where they were converted to carbon targets by the following procedure. The  $\text{CO}_2$  was reacted with lithium at  $850^\circ\text{C}$  to form lithium carbide. Distilled water was added to the lithium carbide to form acetylene, which was dried by freezing out the water vapor. The acetylene was then placed in a cracking cell where it was dissociated by a 1 kilovolt 60 Hz AC discharge and the carbon was deposited onto two aluminum electrodes. The carbon-coated electrodes were used for the accelerator ion source targets as 3 mm disks. Approximately 300 micrograms of carbon are deposited on each electrode in 12 minutes at acetylene pressures ranging from 11 to 5 torr. This quantity of carbon allows  $^{14}\text{C}/^{12}\text{C}$  ratios to be determined with a 0.6% precision for modern terrestrial carbon in 1.5 hours.

#### Isotope Ratio Measurements

The targets were stored and transferred under vacuum and loaded into a target holder. One holder carried 3 lunar targets, one carrier gas target and two NBS Oxalic Acid I standards. Other target holders with duplicate targets were also used. A cesium ion beam of less than 1 mm in diameter sputtered negative carbon ions from the source target. The target moved in a programmed sequence so that the cesium beam sampled 16 different points on the target surface. From each target point,  $^{12}\text{C}$  and  $^{13}\text{C}$  ions were

selected for 0.5 seconds and accelerated to the 2.0 megavolt terminal,  $^{14}\text{C}$  ions were then selected for 20 seconds, followed again by  $^{12}\text{C}$  and  $^{13}\text{C}$  ions for 0.5 seconds. The negative ions were stripped of several electrons at the terminal by passing through a gas stripping canal and accelerated further. Charge state +3, 8 MeV ions were selected by an electric analyzer. The  $^{12}\text{C}$  and  $^{13}\text{C}$  ions passed through one high energy spectrometer magnet into Faraday cups where their currents were measured. The  $^{14}\text{C}$  ions passed through another high energy spectrometer magnet into a low-pressure gas filled ionization chamber, which has nearly 100% collection efficiency.

The carbon from the four lunar samples was measured twice (two targets) and the carbon from the carrier  $\text{CO}_2$  was measured six times. The measured  $^{13}\text{C}/^{12}\text{C}$  ratios represent the combined effect of natural, sample preparation and sputtering fractionation and the  $^{14}\text{C}/^{12}\text{C}$  ratios were corrected for this fractionation to a base of  $\delta^{13}\text{C} = -25$  per mil [Beukens et al., 1986]. The  $^{14}\text{C}/^{12}\text{C}$  ratios were measured relative to the NBS Oxalic Acid I standard ( $1.175 \times 10^{-12}$ ) and were converted to absolute ratios using the absolute activity of this standard, determined by Karlen et al. [1964]. The averages of these measurements are given in Column 4 of Table 1; the errors are 1 $\sigma$  errors. The fifth column gives the  $^{14}\text{C}/^{12}\text{C}$  ratios of the samples (minus carrier) assuming a  $\delta^{13}\text{C}$  of -43.3 per mil for the carrier and the sample. The last column gives the  $^{14}\text{C}/^{12}\text{C}$  ratios of the samples (minus carrier) assuming a  $\delta^{13}\text{C}$  of 0 for the samples and -43.3 per mil for the carrier. A comparison of the last two columns indicates that a large change in the  $\delta^{13}\text{C}$  of the samples produces little change in the  $^{14}\text{C}/^{12}\text{C}$  ratio.

Table 2 summarizes the results for the four temperature fractions, including the  $\text{CO}_2$  released and the equivalent carbon weights. The fourth

column represents the measured  $^{14}\text{C}/^{12}\text{C}$  ratios averaged over the last two columns of Table 1. The fifth column gives the  $^{14}\text{C}$  activity of the soil in decays per minute per kilogram lunar soil (dpm/kg) as calculated from the released carbon, the measured  $^{14}\text{C}/^{12}\text{C}$  ratios and the physical halflife of 5730 years. The errors represent only the 1 $\sigma$  errors due to the accelerator measurements (counting error on  $^{14}\text{C}$  and errors in the  $^{12}\text{C}$  and  $^{13}\text{C}$  current measurements) and do not include the errors in the sample and carrier gas volumes. For a direct comparison, Fireman's [1978] values are given in the last column. His errors are the 1 $\sigma$  statistical counting errors for approximately 3 months of counting time. The comparison of the last two columns shows that the accuracy obtained in 2 hours of running time with the accelerator was 20 times better than obtained with 3 months of beta counting.

#### Results

As seen in the fourth column of Table 2, the  $^{14}\text{C}/^{12}\text{C}$  ratios rise with increasing release temperatures, reaching  $2.63 \times 10^{-12}$  at 1000°C, which is 2.24 times the modern value. The  $^{14}\text{C}/^{12}\text{C}$  ratios less than modern can be explained by a mixture of dead (zero carbon-14) solar wind implanted carbon with modern terrestrial carbon contamination in the soil 10084.937. The  $^{14}\text{C}/^{12}\text{C}$  ratio of 2.24 times the modern value requires that the implanted solar wind carbon has at least the  $^{14}\text{C}/^{12}\text{C}$  ratio of  $2.63 \times 10^{-12}$ .

The amount of carbon, 1.36 mg, obtained from 1.00 g of lunar soil 10084.937 is higher than expected, if lunar soils contain 300 ppm or less of carbon. It therefore appears that this soil sample is contaminated with terrestrial carbon. In stepwise temperature extractions, one would expect the release of the contamination carbon to decrease with increasing temperature. The fact that the  $^{14}\text{C}/^{12}\text{C}$  ratios rise with increasing

temperatures indicates that the terrestrial contamination is mainly ancient (dead) carbon and the lunar carbon is active.

Fireman [1978] obtained significant  $^{14}\text{C}$  activities in the 800°C and 1000°C temperature releases from the small grain size fractions ( $\leq 37\mu\text{m}$ ) of lunar soil 10084. He attributed these activities to solar wind implanted  $^{14}\text{C}$ . The last column of Table 2 shows that he did not observe  $^{14}\text{C}$  activity in 74 to  $125\mu\text{m}$  grain size fraction of 10084 soil. Our results are consistent with his for the 400, 600°C results, slightly higher for the 800°C results and significantly higher for the 1000°C results.

In view of the scientific significance of solar wind with a  $^{14}\text{C}/^{12}\text{C}$  of  $\geq 2.63 \times 10^{-12}$  and also the high precision presently available with the Toronto accelerator mass spectrometer, a carbon isotopic composition versus release-temperature study for a complete set of grain-size fractions from a lunar surface and a subsurface soil sample should be undertaken.

#### Acknowledgements

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TABLE 1.  $^{14}\text{C}/^{12}\text{C}$  Ratios in Stepwise Temperature Carbon Releases  
from Lunar Soil 10084.937 (74-125 Micron Grain Size)

Sample	Sample	Carrier	$(^{14}\text{C}/^{12}\text{C})$	$(^{14}\text{C}/^{12}\text{C})^*$	$(^{14}\text{C}/^{12}\text{C})^{\dagger}$
	Volume $\text{cm}^3$ (STP)	Volume $\text{cm}^3$ (STP)	with carrier $(\times 10^{-14})$	without carrier $(\times 10^{-12})$	without carrier $(\times 10^{-12})$
Carrier $\text{CO}_2$	17.80		$0.382 \pm 0.031$		
400°C	0.50	8.00	$3.49 \pm 0.09$	$0.512 \pm 0.015$	$0.515 \pm 0.015$
600°C	0.52	8.00	$3.83 \pm 0.08$	$0.548 \pm 0.013$	$0.551 \pm 0.014$
800°C	0.77	7.64	$8.35 \pm 0.14$	$0.842 \pm 0.015$	$0.849 \pm 0.015$
1000°C	0.22	8.29	$7.43 \pm 0.15$	$2.627 \pm 0.055$	$2.633 \pm 0.055$

\* Normalized with  $\delta^{13}\text{C} = -43.3$  per mil for the carrier  $\text{CO}_2$  and sample  $\text{CO}_2$ .

† Normalized with  $\delta^{13}\text{C} = -43.3$  per mil for the carrier  $\text{CO}_2$  and  $\delta^{13}\text{C} = 0$  for the sample  $\text{CO}_2$ .

TABLE 2. Total Carbon and  $^{14}\text{C}/^{12}\text{C}$  Ratios in Stepwise Temperature Carbon Releases from 1 Gram of Lunar Soil 10084.937

Extraction Temperature (°C)	Released $\text{CO}_2$ $\text{cm}^3$ (STP)	Released Carbon (mg)	$^{14}\text{C}/^{12}\text{C}$ ( $\times 10^{-12}$ )	$^{14}\text{C}$ Activity (dpm/kg)	Fireman [1978] $^{14}\text{C}$ Activity (dpm/kg)
400	0.95	0.51	$0.513 \pm 0.015$	$3.02 \pm 0.09$	$2.2 \pm 1.2$
600	0.60	0.32	$0.550 \pm 0.014$	$2.04 \pm 0.05$	$2.4 \pm 1.2$
800	0.77	0.41	$0.845 \pm 0.015$	$4.03 \pm 0.07$	$1.5 \pm 1.2$
1000	0.224	0.12	$2.630 \pm 0.055$	$3.65 \pm 0.08$	$-0.2 \pm 1.2$

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ATTACHMENT 2